Chemo-physical Analysis and Molecular Dynamics (MD)
Simulation of Moisture Susceptibility of Nano Hydrated
Lime Modified Asphalt Mixtures

Hui Yao
Research Associate
Department of Civil and Environmental Engineering
Michigan Technological University
1400 Townsend Drive, Houghton, Michigan, 49931, USA
huiyao@mtu.edu

Qingli Dai, Ph.D.
Assistant Professor
Department of Civil and Environmental Engineering
Michigan Technological University
1400 Townsend Drive, Houghton, Michigan, 49931, USA
qingdai@mtu.edu

Zhanping You, Ph.D., P.E.
Professor
Department of Civil and Environmental Engineering
Michigan Technological University
1400 Townsend Drive, Houghton, Michigan, 49931, USA
zyou@mtu.edu

Abstract: The purpose of this study is to investigate the moisture susceptibility of nano hydrated lime (NHL) modified asphalt mixtures and determine the fundamental factors of moisture damage in asphalt mixtures using the molecular dynamics (MD), as well as analyze the effect that the aging of asphalt binders has on the moisture damage in asphalt mixtures. The NHL was added to the control asphalt to make NHL modified asphalt. The modified asphalt was mixed with aggregates to form NHL modified asphalt mixtures. The tensile strength ratio (TSR) test was used to evaluate the moisture susceptibility of asphalt mixtures. When the TSR test was done, different solutions were used to extract the polar groups from the tested asphalt mixtures, and the polar groups were analyzed using Fourier transform infrared spectroscopy (FTIR) attenuated total reflection (ATR). When asphalt oxidizes, the six functional groups (ketones, carboxylic acids, anhydrides, aldehydes, amides and esters) with the carbonyl group can be found in the polar part of asphalt based on FTIR ATR spectral data and references. The polar groups with the carbonyl group also indicate the oxidation extent of asphalt binders. The FTIR test results indicate that carboxylic acids and ketones were the primary aging products in asphalt, and these two carbonyl groups relate to the rutting resistance and moisture susceptibility of asphalt mixtures. Furthermore, the MD interface systems of asphalt-aggregate and aggregate-water were created, as well as the separated systems (asphalt, water, and aggregates). The essential mechanisms for the moisture susceptibility of asphalt mixtures were explored with MD simulations. The potential energies of the interface systems and each separated system were computed to obtain the adhesion energies of the interface MD models. The differences in adhesion energy between the asphalt-aggregate and aggregate-water systems show that water tends to bond to the aggregate rather than the asphalt. This also explains the displacement of water that occurs in asphalt mixtures when there is moisture damage. In addition, the effect of

asphalt aging on the moisture susceptibility of the asphalt mixture was also analyzed using MD interface models. The MD results demonstrate that the aging group in asphalt is helpful in reducing the moisture damage in asphalt mixtures.

Key words: Asphalt; Nano Hydrated Lime (NHL); Fourier Transform Infrared Spectroscopy (FTIR); Moisture Susceptibility; Aging Effect; Molecular Dynamics (MD); Chemo-physical Analysis; Nano Hydrated Lime; Nano Modified Asphalt; Modified Asphalt

1. Introduction

The oxidation hardens the asphalt and increases the viscosity of the asphalt. The exposure to ultraviolet radiation (UV), oxygen, and heat due to nature are the main causes of asphalt aging. The carbonyl and sulfoxide groups increase in the asphalt as oxidation occurs. The carbonyl groups include ketones, carboxylic acids, anhydrides, aldehydes, amides and esters. During the aging of asphalt, the aromatic components of the asphalt agglomerated and caused a reduction in the mobility and reactivity of the asphalt [1-3]. An earlier study on asphalt aging with oxygen focused on the relationship between the properties of asphalt and the extent of oxidation. Asphaltene is the main component that affects the viscosity of asphalt [4]. Oxidation increased the spatial variations of asphalt on the nanoscale. The aging of asphalt also increased the adhesive and cohesive strengths of the asphalt in the early aging state. This indicates that the resistance to rutting and the moisture susceptibility in asphalt mixtures improved. However, the adhesive and cohesive strengths of the asphalt were not enhanced after aging with the pressure aging vessel (PAV). The micromechanical properties of asphalt were determined by the asphaltene content and the size of the microstructures [5]. In addition, some modifiers have an anti-aging performance, such as crumb rubber with styrene-butadiene-styrene (SBS), and nanomaterials [6, 7].

Modified asphalt binders have been widely used in road construction to improve the performance of pavement. Researchers have been searching for innovative materials to improve the performance of asphalt binders and asphalt mixtures. The use of non-modified nanoclay (NMN) and polymer modified nanoclay (PMN) in the control asphalt binder improved the complex shear modulus (G^*) and viscosity [7-9]. The micro- or nano-sized materials (Nanoclay and carbon microfiber) improved the moisture susceptibility of the modified asphalt mixtures or decreased the potential of moisture damage [10]. The recycled asphalt pavement (RAP) was also used to reduce the moisture susceptibility of the hot mix asphalt (HMA) and warm mix asphalt (WMA) [11-13]. In accordance with the literature review [14-18], hydrated lime improved the moisture susceptibility of asphalt mixtures. The addition of the hydrated lime allowed for the precipitation of calcium ions onto the aggregate surface, making it more favorable to the asphalt binder and improving the binder-to-aggregate adhesion [19, 20]. The hydrated lime was either added into the asphalt directly or into the asphalt mixtures as filler, and both ways were shown to improve the resistance to moisture damage and frost, as well as a resistance to chemical aging [16]. That was the motivation to select the nano hydrated lime (NHL) in this study.

Molecular mechanics is when classical mechanics (Newtonian mechanics) is used to model molecular systems. The appropriate force field is assigned to the molecular systems, and the potential energies of these systems are calculated. The physical movements of atoms and molecules are simulated by the computer program in the Molecular Dynamics (MD) simulation. These atoms and molecules move and interact to mimic the response to external forces or environments. The MD program, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [21], is used to study the interaction between the asphalt and aggregates, as well as the reciprocity between the water and aggregates. Five kinds of MD simulations are usually used

to model the different states in the systems, such as Microcanonical ensemble (NVE ensemble), Canonical ensemble (NVT ensemble), Isothermal-isobaric ensemble (NPT ensemble), Isoenthalpic-isobaric ensemble (NPH ensemble), and Generalized ensembles [22]. The relationship between the asphalt and aggregate was developed, and the asphalt-quartz structure model of the interface was used in the system [23]. The Consistent Valence force field (CVFF_aug) was considered in this simulation to characterize the inter-atom interactions. The shear stress and viscosity were evaluated and acceptable simulation results were obtained using the CVFF_aug force field [23].

In this moisture susceptibility study of asphalt mixtures, the NHL was used to improve the moisture damage in the asphalt mixtures. The polar groups in the NHL modified and control asphalt binder were extracted from the damaged asphalt mixtures and analyzed. The aging effect of asphalt was evaluated on the water damage in asphalt mixtures. The fundamental mechanism of moisture damage in the asphalt mixtures was explored with the MD simulation.

2. Research Objectives

The objectives of this study are to analyze the effect aging of the NHL modified asphalt binders has on the moisture damage in asphalt mixtures, and to understand the fundamental factors or chemical groups in the asphalt, which link to the moisture susceptibility of asphalt mixtures. The functional groups with the carbonyl group in the asphalt can be found to relate to the water damage of asphalt mixtures. The six functional groups (ketones, carboxylic acids, anhydrides, aldehydes, amides and esters) containing the carbonyl group in the asphalt were demonstrated and studied. Furthermore, the molecular dynamics were applied to analyze the relationships and interactions of three interface systems: asphalt-aggregate system, aggregate-

water system and aggregate-asphalt with the carboxylic acid (aging group), as well as the impact of asphalt aging on the moisture damage in asphalt mixtures.

3. Materials and Experimental Design

3.1 Chemistry of carbonyl groups

During asphalt oxidation, the six functional groups with the carbonyl group are formed including carboxylic acids, aldehydes, amides, anhydrides, esters, and ketones. 1) Carboxylic acid in the organic compound consists of a carboxyl group ($\text{C}(\text{O})\text{OH}$) and R (the rest of the molecules) [24], and it is easily detected and identified by the FTIR. Carboxylic acid is a weak acid and can only donate H^+ cations [25]. 2) Ketones are the organic components with the structure of $\text{RC}(=\text{O})\text{R}'$, where the R and R' are the hydrocarbon groups. They do not have a reactive group due to their structures [25]. The ketone carbon is often demonstrated as being “ sp^2 hybridized” (electron and molecular structures), and ketones are trigonal and planar around the ketonic carbons. The ketones are different from the functional groups with a carbonyl group, such as carboxylic acids, amides, and esters [26]. 3) Anhydrides consist of two acyl groups ($\text{RCO}-$, carbonyl and alkyl groups) connected to the oxygen atom in the acid anhydrides [24]. It is also a reactive acyl group, so it can produce carboxylic acid and acetate esters [27]. 4) Aldehydes are also an organic group with the structure R-CHO . This structure is called the formyl group when the R is replaced by H. The sp^2 -hybridized and planar carbon connects oxygen with a double bond. The aldehydes and carboxylic acids can be produced from the oxidations of alcohol, and they are polar groups [24, 28, 29]. 5) Amides are a group with the structure $\text{R}_n\text{EO}_x\text{NR}'_2$, where E represents different elements and n and x denote the number of atoms [24]. Amide can be the hydrogen bond acceptor and donor, due to the carbonyl bond. This characteristic of the hydrogen bond acceptor and donor also makes it soluble in water [30]. 6)

Esters are chemical compounds with the structure $\text{RCO}_2\text{R}'$, where R and R' are the hydrocarbons in the organic esters. Esters can be derived from the condensation of the carboxylic acids, such as formate, hexyl octanoate and acetate. The reactions include alcoholysis of acyl chlorides and acid anhydrides, esterification of carboxylic acids, and so on [24, 31-33].

3.2 Preparation of polar groups in the asphalt

The control asphalt used was a PG 58-28 asphalt binder. Nano hydrated lime (NHL) with a particle size of 100nm (Figure 1a) was shipped from, Sha Highland Network Tech Company of China, in Shanghai city. The micro-image of NHL was observed by the field emission scanning electron microscopy (FE-SEM). In Figure 1b, the NHL materials were agglomerated. The NHL consists of 90% calcium hydroxide, 3% calcium carbonate, 1.5% calcium oxide, 1.5% silicon dioxide and some insoluble matters. The density of NHL is 2.24 g/cm^3 . Amounts of 10% and 20% NHL by weight of asphalt were added to the control asphalt.

The NHL material was slowly added into the control asphalt and the modified asphalt binders were blended for two hours in the high shear machine. The asphalt binders and aggregates were blended in the drum mixer and compacted by a Superpave Gyratory Compactor (SGC). Then, the indirect tensile test of asphalt mixtures was performed, and the tensile strength ratio (TSR) of asphalt mixtures was evaluated. When the TSR test was done, the tested samples were immersed and extracted by different solutions. Firstly, the cyclohexane solution was used to extract the non-polar part of the asphalt in the tested asphalt mixtures. Then, the toluene and ethanol were mixed at a ratio of 9:1 to dissolve the remaining part of the asphalt mixture samples. The non-polar and polar parts of the asphalt were obtained through these steps.

Figure 1. Appearance and FE-SEM image of nano hydrated lime materials: a) white powder, b) the FE-SEM image at the magnitude of 1,000x

3.3 Polar group analysis

Infrared spectrometry (IR) is a useful tool in analyzing the chemical composition and molecular bonds of materials. The Fourier Transform Infrared Spectroscopy (FTIR) is a piece of technical equipment used for detecting the infrared absorption of tested materials with a wide range of wavelengths. The FTIR attenuated total reflection (ATR) was used to test different types of samples [34]. The organic asphalt is composed of 90% carbon and hydrogen, and small amounts of other elements [35]. It is known that six movements in the CH_2 groups are common in organic materials, such as symmetrical stretching, rocking, anti-symmetrical stretching, twisting, scissoring, and wagging [36]. Of these movements, the symmetrical and anti-symmetrical stretching movements are most common in asphalt. The Jasco IRT 3000 FTIR spectrometer was employed to test the samples. The non-polar and polar parts of asphalt were tested by FTIR ATR, and the spectra of samples were analyzed.

4. Moisture Susceptibility Test of NHL Modified Asphalt Mixtures

The NHL was slowly added to the PG 58-28 asphalt and the modified asphalt was mixed in the high shear mixer at 135°C and 5000rpm. Due to the high amount of NHL in the asphalt, the shear speed was increased slightly when the sample was blended. The modified asphalt binders were prepared for the asphalt mixture after about two hours of mixing. The aggregates were also pre-heated for approximately two hours to dry. The gradation 5E3 of aggregates was also used to compact the asphalt mixtures by a SGC. The mixing and compaction temperatures were 150°C and 135°C, respectively. Mixing was followed by the Superpave compaction, and the loose asphalt mixtures were heated in the oven (135°C) for at least two hours. The samples were cured at room temperature for at least 72 hours after the asphalt mixtures were compacted.

When the asphalt mixtures were ready, the indirect tensile test was conducted and the tensile strength ratios (TSR) of the control and modified asphalt mixtures were evaluated. The test was based on AASHTO's procedure T283. The air voids were maintained between 6% and 8%. The height of the sample was about 63.5 mm and the diameter was about 100 mm. The thaw cycles were applied to the asphalt mixtures by immersing the sample in the 60°C water for different periods of time. All of the samples were measured, using the Universal Testing Machine (UTM), for the indirect tensile strength and its ratio under the conditions of the room temperature and constant loading rate. These parameters were calculated by equation (1), and the results are shown in Figure 2.

$$S_t = \frac{2P}{\pi tD}, \text{ TSR} = \frac{S_2}{S_1} \quad (1)$$

Where S_t is the tensile strength (Pa), P is the maximum load (N), t is the sample thickness (mm), D is the sample diameter (mm), TSR is the tensile strength ratio, S_1 is the average dry tensile strength, and S_2 is the average conditioned tensile strength.

Figure 2. Tensile strength ratio (TSR) of the control and NHL modified asphalt mixtures

Figure 2 shows the tensile strengths of the control and NHL modified asphalt mixtures. The results show that the addition of NHL into the asphalt mixtures decreases the dry tensile strength, as well as the wet tensile strength. The results also coincide with the trend of the reference [15]. However, the TSR of nano hydrated lime modified asphalt mixtures increases slightly. The moisture susceptibility of nano hydrated lime modified asphalt mixtures improves relative to the control asphalt binder from the TSR data. The wet tensile strength of the control asphalt mixture decreases faster than that of hydrated lime modified asphalt mixtures. Meanwhile, the dry tensile strength at 3 days for the hydrated lime modified asphalt mixtures increases compared to the dry tensile strengths at 2 days. This indicates that the addition of the nano hydrated lime delays the moisture damage of modified asphalt mixtures. The calcium ions from the NHL can prevent the displacement of water at the asphalt binder-aggregate interfaces.

Seen from the reference [15], if the hydrated lime was blended with the asphalt prior to the asphalt mixture, it can effectively reduce the moisture damage of modified asphalt mixtures. In addition, the trends of mixing and compaction temperatures of the control and modified asphalt mixtures were followed by the temperatures of the control asphalt mixture. If the mixing and compaction temperatures and the oxidation time of modified asphalt increases, the strengths of modified asphalt mixtures increase more, as expected. This also explains the low values for strengths of the dry and wet NHL modified asphalt mixtures compared to the control mixture.

5. FTIR Sample Preparation and Characterization Results

The asphalt mixture samples were tested by UTM and the tensile strength of the asphalt mixtures was measured. The tested samples were dried at room temperature. Then, a small amount (around 20 grams) of the tested samples was soaked in cyclohexane solution (around 100 ml). The non-polar compounds in the asphalt melted in the cyclohexane. The first extraction of the asphalt mixtures was done after the solution was mixed for about half an hour and settled for a half hour. The second extraction of the asphalt mixtures was performed using the solvent (around 40 ml) mixed with toluene-ethanol at a ratio of 9:1. The polar components in the asphalt were absorbed by the solvent, not by the cyclohexane. The solution was also mixed for about half an hour and settled for a half hour. The weights of the samples and solutions were recorded, as well as the non-polar and polar parts of the asphalt. The weight of the polar components of the asphalt comprised less than 2% of the weight of the tested asphalt mixtures.

5.1 Functional components in the asphalt

The polar components of the control asphalt were tested at the liquid state by the FTIR ATR. The spectrum data of the polar parts of the control asphalt was analyzed to show the

number of carbonyl groups in the asphalt. The evidence of six functional groups with a carbonyl group was found from the spectral images and references. The polar parts of the asphalt in the solution were examined by FTIR ATR, and the FTIR results are shown in Figure 3. In addition, the carbon-oxygen (C-O) single bond can be observed in the ethanol spectrum [37-39]. One of the solutions used in the FTIR ATR test was mixed with toluene and ethanol, and the bonding features of toluene and ethanol are shown in the spectra of the solution (Figure 3). The features of six functional groups with carbonyl are as follows.

- 1) There are different types of ketones, such as acyclic, cyclic, α , β -unsaturated, and aryl ketone. The ketones can be detected at a range of 1665 cm^{-1} - 1850 cm^{-1} [40, 41], shown in Figure 3a. Ketones can reinforce the intensity of the carbonyl group in asphalt at around 1700 cm^{-1} [2]. They also have a close relationship to the performance of asphalt binders and mixtures [15-17, 42].
- 2) Three bonds, carbon-oxygen double stretching bond (C=O), carbon-oxygen single stretching bond (C-O), and oxygen-hydrogen bond (O-H), are observed in carboxylic acid [40, 41]. Figure 3a shows that the C=O peak of carboxylic acids is detected at a range of 1700 cm^{-1} - 1725 cm^{-1} [7] in the polar groups of asphalt. Figure 3b and Figure 3c demonstrate the peaks of the carbon-oxygen single stretching bond (C-O) and hydroxyl group (O-H) are observed at a range of 1210 cm^{-1} - 1320 cm^{-1} and 2500 cm^{-1} - 3300 cm^{-1} , respectively. The carboxylic acids in the asphalt were also studied by Campbell [2], and the results show that carboxylic acids are also aging products of asphalt.
- 3) Figure 3a shows that two main carbonyl groups are detected at the bands [40, 41] around 1800 cm^{-1} - 1830 cm^{-1} and 1740 cm^{-1} - 1775 cm^{-1} , respectively. The anhydrides are also produced during the oxidation of asphalt and the two carbonyl groups observed should be

anhydrides. A limited anhydrides were observed during oxidation, but large amounts of anhydrides were detected in the long-term aged asphalt [43]. Stronger absorbance appeared at a range of 1740 cm^{-1} - 1775 cm^{-1} , and this peak area was used to represent the anhydrides in this study.

4) The references [40, 41] display that there are two obvious bonds, carbonyl ($\text{C}=\text{O}$) and carbon-hydrogen bonds (C-H), in the aldehydes. The peak of the carbonyl group in the aldehyde is detected at a range of 1720 cm^{-1} - 1740 cm^{-1} , as shown in Figure 3a. It is easy to identify two peaks of carbon-hydrogen bonds of organic materials at a range of 2820 cm^{-1} - 2850 cm^{-1} and 2720 cm^{-1} - 2750 cm^{-1} in Figure 3c. Campbell studied asphalt oxidation, and the results reveal that the aldehydes also increased the carbonyl absorbance in the oxidized asphalt [2].

5) The carbon-oxygen double stretching bond ($\text{C}=\text{O}$) and carbon-oxygen single stretching bond (C-O) are observed in the ester group [40, 41]. The peak of the carbonyl group ($\text{C}=\text{O}$) of esters is found in a region of 1735 cm^{-1} - 1750 cm^{-1} from Figure 3a in the polar part of the asphalt. The peak of the carbon-oxygen single bond (C-O) in the esters can be detected in an area of 1000 cm^{-1} - 1300 cm^{-1} from Figure 3b. Due to the small amount of esters in the oxidized asphalt, there is a limited contribution to the aging of the asphalt [2].

6) Figure 3a reveals that the peak of carbonyl groups ($\text{C}=\text{O}$) in the amide is observed at a range of 1640 cm^{-1} - 1690 cm^{-1} . Figure 3b and Figure 3c also show that the N-H stretching and bending bonds are found in a region of 3100 cm^{-1} - 3500 cm^{-1} (including a shoulder band) and 1550 cm^{-1} - 1640 cm^{-1} , respectively, in the asphalt at the liquid state. Due to the small amount of amide [2] in the asphalt, the amide may not be easily detected.

(a) Functional groups containing the carbonyl group in the polar asphalt (liquid state)

(b) Nitrogen-hydrogen and carbon-oxygen bonds in the polar asphalt (liquid state)

(c) Oxygen-hydrogen and Nitrogen-hydrogen bonds in the polar asphalt (liquid state)

Figure 3. Chemical bonds in the asphalt binders

5.2 FTIR results of polar groups in the control and NHL modified asphalt

After identifying the functional groups in the polar parts of the control asphalt, the liquid asphalt samples were dropped into the groove of FTIR and tested by FTIR ATR. The FTIR spectra were recorded with the accumulation of 256 scans, with a resolution of 4cm⁻¹. The peak range of functional polar carbonyl groups in the asphalt is demonstrated in Table 1. The polar compounds were tested by the FTIR ATR at liquid state. The results of the FTIR spectra are shown in Figure 4. The carbonyl groups in the polar part of the asphalt were analyzed, and these groups may relate to the performance of the asphalt mixtures [15].

Table 1. Functional groups containing a carbonyl in the asphalt binder

Functional Groups	Absorption Frequency Region, Wavenumber (cm ⁻¹)
Carbonyl: C=O	1670-1820, stretching vibration, strong intensity [40, 41, 44]
Functional Groups: Carboxylic Acid	
C=O	1700-1725, stretching vibration [40, 41, 44]
O-H	2500-3300, stretching vibration, strong intensity [40, 41, 44]
C-O	1210-1320, stretching vibration, strong intensity [40, 41, 44]
Functional Groups: Aldehyde	
C=O	1720-1740, stretching vibration, strong intensity [40, 41, 44]
=C-H	2820-2850 & 2720-2750, stretching vibration, medium intensity [40, 41, 44]
Functional Groups: Amide	
C=O	1640-1690, stretching vibration, strong intensity [40, 41, 44]
N-H	3100-3500, stretching vibration, unsubstituted [40, 41]
N-H	1550-1640, bending vibration [40, 41]
Functional Groups: Ketone	
Acyclic	1705-1725, stretching vibration, strong intensity [40, 41]
Cyclic	3-membered-1850, stretching vibration, strong intensity [40, 41]
	4-membered-1780, stretching vibration, strong intensity [40, 41]
	5-membered-1745, stretching vibration, strong intensity [40, 41]
	6-membered-1715, stretching vibration, strong intensity [40, 41]
	7-membered-1705, stretching vibration, strong intensity [40, 41]
α , β - unsaturated	1665-1685, stretching vibration, strong intensity [40, 41]
Aryl ketone	1680-1700, stretching vibration, strong intensity [40, 41]
Functional Groups: Anhydride	
C=O	1800-1830&1740-1775, stretching vibration [40, 41, 44]
Functional Groups: Ester	
C=O	1735-1750, stretching vibration, strong intensity [40, 41, 44]
C-O	1000-1300, stretching vibration, two bands or more [40, 41, 44]

(a) FTIR spectra of the polar parts in the control asphalt at a range of 1500-2000 cm^{-1}

(b) FTIR Spectra of the polar parts in 10% NHL modified asphalt at a range of 1500-2000 cm^{-1}

(c) FTIR spectra of the polar parts in 20% NHL modified asphalt at the range of 1500-2000cm⁻¹

Figure 4. FTIR results of polar parts in the asphalt binders

Figures 4 shows the FTIR spectra of polar compounds in the asphalt at the liquid state. The solvents used were also tested with the FTIR ATR. The FTIR spectra of the control and NHL modified asphalt were compared, and the polar compositions in the asphalt were analyzed. Based on the literature review [15-17], the hydrated lime can enhance the adhesion between the aggregate and asphalt. The hydrated lime particles melted in the asphalt and the carboxylic acids/carbonyl groups in the asphalt improved the moisture susceptibility of the asphalt mixtures including the mixture with siliceous aggregates. Compared to the spectra of the solutions, the peaks of the functional polar groups in asphalt were clearly displayed (section: functional group components). The ratios of carbonyl groups in the asphalt were calculated using equation (2)

313 through equation (8). The results of the ratio calculations of the control and NHL modified
 314 asphalt at the liquid state are shown in Figure 5.

$$315 \quad I_{\text{acids}} = \frac{\text{Area of the carboxylic acid bands between } 1720 \text{ cm}^{-1} \text{ and } 1700 \text{ cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000 \text{ cm}^{-1} \text{ and } 600 \text{ cm}^{-1}} \quad (2)$$

$$316 \quad I_{\text{aldehydes}} = \frac{\text{Area of the aldehyde bands between } 1735 \text{ cm}^{-1} \text{ and } 1720 \text{ cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000 \text{ cm}^{-1} \text{ and } 600 \text{ cm}^{-1}} \quad (3)$$

$$317 \quad I_{\text{amides}} = \frac{\text{Area of the amide bands between } 1660 \text{ cm}^{-1} \text{ and } 1645 \text{ cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000 \text{ cm}^{-1} \text{ and } 600 \text{ cm}^{-1}} \quad (4)$$

$$318 \quad I_{\text{anhydrides}} = \frac{\text{Area of the anhydride bands between } 1775 \text{ cm}^{-1} \text{ and } 1750 \text{ cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000 \text{ cm}^{-1} \text{ and } 600 \text{ cm}^{-1}} \quad (5)$$

$$319 \quad I_{\text{esters}} = \frac{\text{Area of the ester bands between } 1750 \text{ cm}^{-1} \text{ and } 1735 \text{ cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000 \text{ cm}^{-1} \text{ and } 600 \text{ cm}^{-1}} \quad (6)$$

$$320 \quad I_{\text{aryl ketones}} = \frac{\text{Area of the aryl ketone bands between } 1700 \text{ cm}^{-1} \text{ and } 1685 \text{ cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000 \text{ cm}^{-1} \text{ and } 600 \text{ cm}^{-1}} \quad (7)$$

$$321 \quad I_{\alpha, \beta \text{ unsaturated ketones}} = \frac{\text{Area of the } \alpha, \beta \text{ unsaturated ketone bands between } 1680 \text{ cm}^{-1} \text{ and } 1665 \text{ cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000 \text{ cm}^{-1} \text{ and } 600 \text{ cm}^{-1}} \quad (8)$$

(a) Ratio calculations of functional polar groups in the control and NHL modified asphalt at the dry condition (liquid state)

(b) Ratio calculations of functional polar groups in the control and NHL modified asphalt after a 2-day wet condition (liquid state)

(c) Ratio calculations of functional polar groups in the control and NHL modified asphalt after a 3-day wet condition (liquid state)

Figure 5. Ratio calculations of functional polar groups in the control and NHL modified asphalt

During the FTIR sample preparations, it is possible that the concentrations of polar groups in the asphalt were affected by the solutions. However, the trends of these functional groups were not changed. It is likely that the composition produced by the asphalt oxidation may be changed by different conditions. Figure 5a shows the ratios of functional polar groups in the control and NHL modified asphalt at the dry condition. The amount of anhydride is the highest in the polar groups in the asphalt. If the sum of aryl ketones and α,β -unsaturated ketones are considered as ketones, then, the ketones are the main products in the functional polar groups of asphalt. After the asphalt mixture tests, it is determined that the carboxylic acids in the polar groups of asphalt are also a major part of the asphalt oxidation products. The amount of esters, aldehydes and amides is less than the three primary groups (anhydrides, ketones and carboxylic acids) in the oxidized asphalt. Seen from Figure 5a, the amounts of functional carbonyl groups in

the 20% NHL modified asphalt are more than the control and the 10% NHL modified asphalt. The quantity of carbonyl groups in the 10% NHL modified asphalt is slightly more than that of the control asphalt. The addition of NHL into the control asphalt increases the functional groups in the modified asphalt in the dry condition.

Figure 5b and Figure 5c reveal the ratios of the functional groups in the control and NHL modified asphalt after 2- and 3- day wet conditions. The amount of carbonyl groups in the 20% NHL modified asphalt is more than those in the control and 10% NHL modified asphalt, and the quantity of carbonyl groups in the 10% NHL modified asphalt is more than that of the control asphalt under the wet condition. The anhydrides, carboxylic acids and ketones are still the leading products during the aging process in the polar asphalt at a liquid state. Considering the TSR results of the control and NHL modified asphalt mixtures, the more polar groups that are in the asphalt, the better the TSR results are. This indicates that asphalt aging under the wet condition helps the asphalt mixture to resist moisture damage, especially the ketones, carboxylic acids, and anhydride in this case. The calcium ions in the NHL modified asphalt may be the reason for the improvement of the moisture damage in the asphalt mixtures.

Therefore, the ketones and carboxylic acids increased more after the oxidation of asphalt, and the anhydrides and amides increased, in this case. The aging groups in the asphalt enhance the resistance to permanent deformation in the asphalt pavement at an earlier stage and also help to improve the moisture susceptibility of asphalt mixtures. Furthermore, the effect of NHL materials on the resistance to moisture damage in asphalt mixtures is positive.

6. Molecular Dynamics (MD) Analysis

The bonding strength between the aggregates and the asphalt determines the performance of the rutting resistance and moisture susceptibility in asphalt mixtures [9, 45]. The mechanism of water replacement in the moisture damage in asphalt mixtures is demonstrated in Figure 6, from the initiation to the propagation stage. The bonding strength is related to the adhesion energy between the asphalt and aggregates, which varies with the interfacial interactions among asphalt, water, and aggregates. Therefore, the adhesion energy calculation is important to explain the mechanism of moisture distresses in the asphalt mixtures. In this study, the interaction between the asphalt and aggregates, as well as the interaction between the water and aggregates, was first simulated using the molecular dynamics method. Through MD simulations of the potential energies of the interface and individual models, the adhesion energies were computed to explain the cause of moisture damage in asphalt mixtures. The aging effects of asphalt binders were demonstrated for the mitigation of water damage in asphalt mixtures.

Figure 6. Stages of water displacement in the moisture damage of asphalt mixtures

When the asphalt and aggregates are mixed, the aggregates are heated in the oven for at least two hours. It is assumed that water on the surface or in the porous holes of the aggregates is vaporized and escapes from the aggregates. This confirms that the water inducing the damage in the asphalt mixtures is from the external environment. The repeated traffic loads and changes in environmental conditions decrease the strength of adhesion between the aggregates and

asphalt/asphalt mastic and the cohesive bonding strength within the asphalt binder [46, 47]. It is also assumed that the asphalt mastic consists of the asphalt binder and fine aggregates (aggregate size is normally smaller than 2.36 mm), and the asphalt mastic is in the transition state to form the asphalt mixtures [48, 49]. When the adhesive and cohesive bonds are reduced in the asphalt mixtures, water starts to intrude into the aggregates, and moisture damage in asphalt mixtures develops from the initiation stage to the propagation stage (Figure 6).

In these interface models, the crystal quartz (SiO_2) structure is represented as the aggregate in the asphalt mixtures. Based on the Corbett method [35], the asphalt material is composed of asphaltenes, polar aromatics, naphthene aromatics, and saturates through different absorption and desorption. Based on the references [50, 51], the asphalt model consists of asphaltenes, saturates, and aromatics at the ratio of 5:41:27, respectively. The structure of asphaltenes in the asphalt model was proposed by Artok et al. [52] and Zhang et al. [53]. These saturates were represented by docosane molecules and the aromatics were replaced by the 1, 7-dimethylnaphthalene in the asphalt model from the references [53-56]. In addition, based on the structure of asphalt components from the references [53], the aging effects on these components were investigated and one of the asphalt aging groups (the carboxylic acid group) was attached in the structure of the components (Figure 7). The possible structures of asphaltenes (Figure 7a) and aromatics (Figure 7b) with the carboxylic acid group are proposed and displayed in Figure 7. However, the structure of docosane (Figure 7c) is relatively stable, and it is likely that the docosane is not compatible with other oxidizing agents.

Three interface models among the asphalt, water, and aggregates were created by the Materials Processes and Simulations (MAPS) software with the Amber Cornell Extension Force Field [57, 58]. These interface models include the interaction systems of 1) asphalt-aggregate, 2)

aggregate-water, and 3) aggregate-asphalt with carboxylic acid (aging group) (Figure 8). The density of asphalt in the interface model is around 1.04 g/cm³, which matches the physical properties of asphalt. Parts of bond parameters of the Amber Cornell Extension Force Field are from the Amber Cornell Force Field and General Amber Force Field (GAFF) [57, 58]. The system energy formula in the Amber Cornell Extension Force Field is shown in equation (9).

$$E_{total} = \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_\theta (\theta - \theta_{eq})^2 + \sum_{dihedrals} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)] + \sum_{i < j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} + \frac{q_i q_j}{\epsilon R_{ij}} \right] \quad (9)$$

Where the first term is the energy between the covalently bonded atoms; the second term is the energy caused by the geometry of electron orbitals; the third term is the energy from twisting a bond; the fourth term is a non-bonded energy from van der Waals and electrostatic energies (atom pairs). r_{eq} and θ_{eq} are the equilibrium structural parameters; K_r and K_θ are the force constants; n is the multiplicity and γ is the phase angle for the torsional angle parameters; A , B and q are the non-bonded potentials between all atom pairs; and finally, R_{ij} is the distance of atoms and ϵ is the well depth for van der Waals energy.

In the interaction models, the Electrostatic Potential (ESP) charges were allotted to the asphalt components by using the quantum mechanics module NWChem in the MAPS software [59]. The Conjugate Gradient method and the Particle Mesh Ewald (PME) method were used to optimize the energy of the system. The Conjugate Gradient method was used to optimize the energy in the large and complex systems. The optimization calculation formula is shown in equation (10).

$$f(x) = \frac{1}{2} x^T A x - x^T b, x \in R^n, (\text{iterations}) \quad (10)$$

Where A is symmetric, positive and real, b is a known coefficient.

PME is an Ewald summation for the long-range potential computation in the periodic systems. In the PME method, the long-range part is divided into two sections: short-range and long-range contributions. The calculations of two-part energies are expressed in equation (11).

$$\varphi(r) \stackrel{\text{def}}{=} \varphi_{sr}(r) + \varphi_{lr}(r) \quad (11)$$

Where $\varphi_{sr}(r)$ is the short-range term potential energy which quickly converges in the real space, and $\varphi_{lr}(r)$ is the long-range term potential which quickly converges in the Fourier space.

(a) asphaltene structure with the carboxylic acid group (aging group)

(b) 1,7-dimethylnaphthalene with the carboxylic acid group (aging group)
(c) Docosane structure, represents a saturate.

Figure 7. Three components in the asphalt model with the carboxylic acid group (aging group)

1) The molecular structures of the asphalt-aggregate system: (a) aggregate-asphalt system; (b) only the asphalt system; and (c) only the aggregate system with functional group OH on the surface layer.

- 2) The molecular structures of the aggregate-water system: (d) aggregate-water system; (e) only the water system; and (f) only the aggregate system with functional group OH on the surface layer.

- 3) The molecular structures of the asphalt-aggregate system with aging groups: (a) aggregate-asphalt system with the carboxylic acid group; (b) only the asphalt system with the carboxylic acid group; and (c) only the aggregate system with functional group OH on the surface layer.

Figure 8. MD models for 1) Asphalt-aggregate interactions; 2) water-aggregate interactions and

3) aggregate-asphalt with the carboxylic acid group systems

Figure 8 shows the interface MD models of asphalt-aggregate, water-aggregate, aggregate-asphalt with the carboxylic acid group systems. The adhesion energy of each system directly relates to the bonding strength of the system. The adhesion energy of each interface system is computed using equation (12).

$$E_{adhesion} = \frac{E_{interface} - (E_{top} + E_{substrate})}{A} \quad (12)$$

Where $E_{adhesion}$ is the adhesion energy of the interface system (kcal/mol); $E_{interface}$ is the potential energy of the interface system (kcal/mol); E_{top} is the potential energy of the top layer system, asphalt, or water system (kcal/mol); $E_{substrate}$ is the potential energy of the substrate system, and aggregate system (kcal/mol); A is the area of each interface system (Angstrom²).

To calculate the adhesive energy for the asphalt-aggregate, an interface model with a specific vacuum layer and periodic boundary condition was applied as shown in Figure 8a. The aggregate model includes a surface layer with the hydroxyl group (-OH) for the following study. The separate aggregate models with the surface function group (-OH) and asphalt model were developed as shown in Figure 8b and Figure 8c. The NVT simulation was conducted in three interface systems and in each separate system. The potential energies of these systems were computed and outputted. The energy conversion factor was used to present the adhesion energy (conversion factor: $1 \frac{kcal}{mol} = 6.95 \times 10^{-21} J$). Avogadro's number was used to convert the energy unit. After computing and unit conversion, the adhesion energy of the asphalt-aggregate system is -0.1446295 J/m². Similarly, the adhesion energy calculation of the water-aggregate interface was conducted with the interface model and two separate systems of the water layer and aggregate substrate, shown in Figure 8d, Figure 8e, and Figure 8f. The adhesion energy of the

aggregate-water system was calculated as -1.86955 J/m^2 . In order to demonstrate the effects of aging on the asphalt, on the adhesion energy interface, the interface model of the aggregate-asphalt with the carboxylic acid group and two separate systems were developed as shown in Figure 8g, Figure 8h, and Figure 8i. The adhesion energy of the aggregate-asphalt with the carboxylic acid group system was evaluated as -0.151371 J/m^2 .

The different adhesion energies of asphalt-aggregate and aggregate-water systems indicate that the bonding strength between the asphalt and aggregate is lower than the attraction force between aggregate and water. The energy difference is also the reason why water bonds to the aggregates easier than the asphalt in asphalt mixtures. Therefore, coating the aggregates with asphalt is the key process in making asphalt mixture samples or paving asphalt pavement. It is also very important to dry the aggregates prior to mixing. These procedures make sure that water completely vaporizes from the aggregate pores and surfaces. These are also preventive measures/practices to reduce the moisture damage in asphalt mixtures. Furthermore, the energy of adhesion of the aggregate-asphalt (with the carboxylic acid group) system is greater than that of the asphalt-aggregate system. The varying energies of two systems imply that the presence of the aging group in asphalt causes a stronger adhesion force between the asphalt and aggregate. This phenomenon also reasonably interprets that studying the mildly aged asphalt is helpful in improving the water susceptibility of asphalt mixtures.

7. Discussions and Conclusions

The control and NHL modified asphalt were tested by FTIR ATR to analyze the polar groups with carbonyl in the asphalt at a liquid state. Parts of the control and the NHL modified asphalt mixture samples tested by TSR were also used to be extracted by solutions. These solutions contained the polar functional groups that were detected by the FTIR ATR to analyze

the carbonyl groups in the asphalt. The mechanical driving forces for water damage between the asphalt-aggregate and aggregate-water systems in asphalt mixtures were explored and discussed using molecular dynamics simulations. Based on the data analysis of the extracted control and the NHL modified asphalt, the following conclusions can be drawn.

1) During the oxidation of asphalt, the resins and maltenes in the asphalt helped to generate polar group components, including carbonyl groups, sulfoxide groups, and nitrogen oxides. Carboxylic acids and ketones were the major products of the oxidized asphalt, which also produces high amounts of anhydrides. The limited amount of amides, esters, and aldehydes in the oxidized and extracted asphalt was detected. Carboxylic acids, ketones and anhydrides are the pivotal components in the asphalt that link to the rutting and moisture resistance in asphalt mixtures, as well as the bonding strength between the asphalt and aggregates. The aging of asphalt definitely improves the resistance to moisture damage in wet environment at an early stage according to these research findings. However, the long-term aging of asphalt causes the degradation of the bonding strength between the asphalt and aggregates, as well as the fatigue life and resistance to moisture.

2) The interface MD models of asphalt-aggregate and aggregate-water systems were generated to simulate the mechanism that produces adhesive energy, and also to mimic the interactions between aggregates and asphalt/water. The potential energies of each MD interface system and separated systems (asphalt, water, and aggregate) were computed to determine the bonding energy of each system. The difference of adhesive energies between the asphalt-aggregate and aggregate-water systems is the fundamental reason for moisture damage in asphalt mixtures. The water tends to adhere to aggregates rather than to asphalt under the same condition. In addition, from investigating the different adhesion energies between the

aggregate and asphalt with or without the carboxylic acid group (aging group), the moderately aged asphalt improves the energy of adhesion and, thus, helps resist moisture damage in asphalt mixtures.

With chemical extraction, the polar and non-polar components in the asphalt were separated and analyzed to link the moisture susceptibility of asphalt mixtures with FTIR characterization. Ketones, carboxylic acids and anhydrides are the main compounds present during asphalt oxidation in this study, and these also relate to the performance of the pavement. MD simulations discovered the adhesion energy difference between asphalt-aggregate and aggregate-water systems. The analysis results explain the chemo-physical properties of asphalt related to the moisture damage in asphalt mixtures. In addition, the future research of our group will focus on simulating asphalt aging.

Acknowledgement

The authors would like to thank Dr. Yoke Khin Yap and Mingxiao Ye for the help on FTIR testing. The authors also appreciate the help of Dr. Andreas Bick on generating the molecular dynamics model. The experimental work was completed at the Transportation Materials Research Center of Michigan Technological University. The authors appreciate the financial support of the U.S. National Science Foundation (NSF) under the grant number: 1300286. Any opinion, finding, and conclusion or recommendation expressed in this material are those of the authors and do not necessarily reflect the view of any organization.

References

[1] Petersen JC, Harnsberger PM, Robertson RE. Factors affecting the kinetics and mechanisms of asphalt oxidation and the relative effects of oxidation products on age hardening. Preprints of Papers, American Chemical Society, Division of Fuel Chemistry 1996;41(4):1232-44.

- [2] Campbell PG, Wright JR. Infrared spectra of asphalts: Some aspects of the changes caused by photooxidation. *Journal of Research of the National Bureau of Standards Section C: Engineering and Instrumentation*. 1964;68C(2).
- [3] Fernandez-Gomez WD, Quintana HR, Lizcano FR. A review of asphalt and asphalt mixture aging. *INGENIERÍA E INVESTIGACIÓN*. 2013;33(1):5-12.
- [4] Caro S, Diaz A, Rojas D, Nuñez H. A micromechanical model to evaluate the impact of air void content and connectivity in the oxidation of asphalt mixtures. *Construction and Building Materials*. 2014;61(0):181-90.
- [5] Yuhong Wang PE, Zhao K, Glover C, Chen L, Wen Y, Chong D, et al. Effects of aging on the properties of asphalt at the nanoscale. *Construction and Building Materials*. 2015;80(0):244-54.
- [6] Xiang L, Cheng J, Kang S. Thermal oxidative aging mechanism of crumb rubber/SBS composite modified asphalt. *Construction and Building Materials*. 2015;75(0):169-75.
- [7] Yao H, You Z, Li L, Goh SW, Lee CH, Yap YK, et al. Rheological properties and chemical analysis of nanoclay and carbon microfiber modified asphalt with Fourier transform infrared spectroscopy. *Construction and Building Materials*. 2013;38(0):327-37.
- [8] You Z, Mills-Beale J, Foley JM, Roy S, Odegard GM, Dai Q, et al. Nanoclay-modified asphalt materials: Preparation and characterization. *Construction and Building Materials*. 2011;25(2):1072-8.
- [9] Yao H, You Z, Li L, Shi X, Goh SW, Mills-Beale J, et al. Performance of asphalt binder blended with non-modified and polymer-modified nanoclay. *Construction and Building Materials*. 2012;35(0):159-70.
- [10] Goh SW, Akin M, You Z, Shi X. Effect of deicing solutions on the tensile strength of micro- or nano-modified asphalt mixture. *Construction and Building Materials*. 2011;25(1):195-200.
- [11] Zhao S, Huang B, Shu X, Woods M. Comparative evaluation of warm mix asphalt containing high percentages of reclaimed asphalt pavement. *Construction and Building Materials*. 2013;44:92-100.
- [12] Zhao S, Huang B, Shu X, Jia X, Woods M. Laboratory performance evaluation of warm-mix asphalt containing high percentages of reclaimed asphalt pavement. *Transportation Research Record: Journal of the Transportation Research Board*. 2012(2294):98-105.
- [13] Shu X, Huang B, Shrum ED, Jia X. Laboratory evaluation of moisture susceptibility of foamed warm mix asphalt containing high percentages of RAP. *Construction and Building Materials*. 2012;35(0):125-30.
- [14] Cheng J, Shen J, Xiao F. Moisture Susceptibility of Warm-Mix Asphalt Mixtures Containing Nanosized Hydrated Lime. *Journal of Materials in Civil Engineering*. 2011;23(11):1552-9.
- [15] Huang S, Robertson R, Branthaver J, Claime Petersen J. Impact of Lime Modification of Asphalt and Freeze–Thaw Cycling on the Asphalt–Aggregate Interaction and Moisture Resistance to Moisture Damage. *Journal of Materials in Civil Engineering*. 2005;17(6):711-8.
- [16] Huang S-C, Miknis FP, Schuster W, Salmans S, Boysen R. Rheological and Chemical Properties of Hydrated Lime and Polyphosphoric Acid Modified Asphalts with Long Term Aging. *Journal of Materials in Civil Engineering, American Society of Civil Engineering (ASCE)*. 2010.
- [17] Lesueur D, Petit J, Ritter H-J. The mechanisms of hydrated lime modification of asphalt mixtures: a state-of-the-art review. *Road Materials and Pavement Design*. 2012;14(1):1-16.

593 [18] Huang B, Shu X, Dong Q, Shen J. Laboratory evaluation of moisture susceptibility of hot-
 594 mix asphalt containing cementitious fillers. *Journal of Materials in Civil Engineering*.
 595 2010;22(7):667-73.

596 [19] Ishai I, Craus J. Effect of the filler on aggregate-bitumen adhesion properties in bituminous
 597 mixtures. *Association of Asphalt Paving Technologists Proc. From the Technical Session, San*
 598 *Antonio, Texas, 21-23 February 1977*1977. p. 228-58.

599 [20] Blazek J, Sebor G, Maxa D, Ajib M, Paniagua H. Effect of hydrated lime addition on
 600 properties of asphalt. *Petroleum and Coal*, 42(1), pp41-45. 2000.

601 [21] Plimpton S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *Journal of*
 602 *Computational Physics*. 1995;117(1):1-19.

603 [22] Bandyopadhyay A. *Molecular Modeling of EPON 862-DETDA Polymer*: Michigan
 604 *Technological University*; 2012.

605 [23] Lu Y, Wang L. Nanoscale modelling of mechanical properties of asphalt–aggregate
 606 interface under tensile loading. *International Journal of Pavement Engineering*. 2010;11(5):393-
 607 401.

608 [24] Chemistry IUoPaA. *Compendium of Chemical Terminology*. Version 2.3 ed: International
 609 *Union of Pure and Applied Chemistry*, 2011.

610 [25] Morrison RTBRN. *Organic chemistry*. Englewood Cliffs,N.J.: Prentice-Hall; 1992.

611 [26] McMurry J. *Organic Chemistry*: Cengage Learning; 2011.

612 [27] Held H, Rengstl A, Mayer D. *Acetic Anhydride and Mixed Fatty Acid Anhydrides*.
 613 *Ullmann's Encyclopedia of Industrial Chemistry*: Wiley-VCH Verlag GmbH & Co. KGaA; 2000.

614 [28] Carey FA, Sundberg RJ. *Advanced Organic Chemistry: Part B: Reaction and Synthesis*:
 615 *Springer*; 2007.

616 [29] Jerry M. *Advanced organic chemistry : reactions, mechanisms and structure*1985.

617 [30] Kemnitz CR, Loewen MJ. “Amide Resonance” Correlates with a Breadth of C–N Rotation
 618 Barriers. *Journal of the American Chemical Society*. 2007;129(9):2521-8.

619 [31] Riemenschneider W, Bolt HM. *Esters, Organic*. *Ullmann's Encyclopedia of Industrial*
 620 *Chemistry*: Wiley-VCH Verlag GmbH & Co. KGaA; 2000.

621 [32] Williams RJ, Gabriel A, Andrews RC. The relation between the hydrolysis equilibrium
 622 constant of esters and the strengths of the corresponding acids. *Journal of the American*
 623 *Chemical Society*. 1928;50(5):1267-71.

624 [33] Neises B, Steglich W. Esterification of Carboxylic Acids with Dicyclohexylcarbodiimide/4-
 625 *Dimethylaminopyridine*: *tert-Butyl Ethyl Fumarate*. *Organic Syntheses*: John Wiley & Sons,
 626 *Inc.*; 2003.

627 [34] Griffiths P, De Haseth JA. *Fourier Transform Infrared Spectrometry*: John Wiley & Sons;
 628 2007.

629 [35] Asphalt Institute. *Superpave Performance Graded Asphalt Binder Specification and Testing*.
 630 *Superpave Series No 1(SP-1)*. Lexington KY, USA2003.

631 [36] Atkins P, de Paula J. *Elements of Physical Chemistry*: OUP Oxford; 2013.

632 [37] NIST Mass Spec Data Center SES, director. "Infrared Spectra" in *NIST Chemistry*
 633 *WebBook*, NIST Standard Reference Database Number 69. Gaithersburg MD, 20899, United
 634 *States*: National Institute of Standards and Technology; 2014.

635 [38] Tomasi RA. *A Spectrum of Spectra*: Sunbelt R & T, Incorporated; 1992.

636 [39] Tomasi RA. *A Spectrum of Spectral Problems: Supplement*: Sunbelt R & T, Incorporated;
 637 1994.

638 [40] Silverstein RM, Bassler GC. Spectrometric identification of organic compounds. Journal of
639 Chemical Education. 1962;39(11):546.

640 [41] Silverstein RM, Bassler GC, Morrill TC. Spectrometric identification of organic compounds.
641 New York: Wiley; 1981.

642 [42] Little DN, Epps JA, Sebaaly PE. Hydrated lime in hot mix asphalt. National Lime
643 Association; 2006.

644 [43] Petersen JC, National Research C, Transportation Research B, Committee on Characteristics
645 of Bituminous M. A review of the fundamentals of asphalt oxidation chemical, physicochemical,
646 physical property, and durability relationships. 2009.

647 [44] Yao H, You Z, Li L, Lee C, Wingard D, Yap Y, et al. Rheological Properties and Chemical
648 Bonding of Asphalt Modified with Nanosilica. Journal of Materials in Civil Engineering.
649 2013;25(11):1619-30.

650 [45] Yao H, Li L, Yang X-l, Dan H-c, Luo S. Mechanics Performance Research and
651 Microstructure Analysis of Nanomaterials Modified Asphalt. Journal of Building Materials.
652 2011;14(5):712-7.

653 [46] Caro S, Masad E, Bhasin A, Little D. Coupled Micromechanical Model of Moisture-
654 Induced Damage in Asphalt Mixtures. Journal of Materials in Civil Engineering.
655 2010;22(4):380-8.

656 [47] Yao H, Liu Y, You Z, Li L, Goh SW. Discrete Element Simulation of Bending Beam
657 Rheometer Tests for Asphalt Binder. International Journal of Pavement Research and
658 Technology. 2012;5(3):161-8.

659 [48] Liu Y, You Z, Dai Q, Mills-Beale J. Review of advances in understanding impacts of mix
660 composition characteristics on asphalt concrete (AC) mechanics. International Journal of
661 Pavement Engineering. 2011;12(4):385-405.

662 [49] Adhikari S, You Z. Investigating the Sensitivity of Aggregate Size within Sand Mastic by
663 Modeling the Microstructure of an Asphalt Mixture. Journal of Materials in Civil Engineering.
664 2011;23(5):580-6.

665 [50] Zhang L, Greenfield ML. Relaxation time, diffusion, and viscosity analysis of model asphalt
666 systems using molecular simulation. The Journal of Chemical Physics. 2007;127(19):1-13.

667 [51] Zhang L, Greenfield ML. Molecular Orientation in Model Asphalts Using Molecular
668 Simulation. Energy & Fuels. 2007;21(2):1102-11.

669 [52] Artok L, Su Y, Hirose Y, Hosokawa M, Murata S, Nomura M. Structure and Reactivity of
670 Petroleum-Derived Asphaltene†. Energy & Fuels. 1999;13(2):287-96.

671 [53] Zhang L, Greenfield ML. Analyzing Properties of Model Asphalts Using Molecular
672 Simulation. Energy & Fuels. 2007;21(3):1712-6.

673 [54] Zhang L, Greenfield ML. Effects of Polymer Modification on Properties and Microstructure
674 of Model Asphalt Systems. Energy & Fuels. 2008;22(5):3363-75.

675 [55] Kowalewski I, Vandenbroucke M, Huc AY, Taylor MJ, Faulon JL. Preliminary Results on
676 Molecular Modeling of Asphaltenes Using Structure Elucidation Programs in Conjunction with
677 Molecular Simulation Programs. Energy & Fuels. 1996;10(1):97-107.

678 [56] Groenzin H, Mullins OC. Molecular Size and Structure of Asphaltenes from Various
679 Sources. Energy & Fuels. 2000;14(3):677-84.

680 [57] Wang J, Wolf RM, Caldwell JW, Kollman PA, Case DA. Development and testing of a
681 general amber force field. Journal of Computational Chemistry. 2004;25(9):1157-74.

682 [58] Cornell WD, Cieplak P, Bayly CI, Gould IR, Merz KM, Ferguson DM, et al. A Second
683 Generation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules.
684 Journal of the American Chemical Society. 1995;117(19):5179-97.
685 [59] Valiev M, Bylaska EJ, Govind N, Kowalski K, Straatsma TP, Van Dam HJJ, et al.
686 NWChem: A comprehensive and scalable open-source solution for large scale molecular
687 simulations. Computer Physics Communications. 2010;181(9):1477-89.